Structural Characteristics of Sulphuric-Acid Graphite Compounds During Electrochemical Intercalation

by

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Introduction

The high electrical conductivity of acceptor graphite intercalation compounds (GICs) arises from holes in the graphitic π bands which are due to charge transfer to the acceptor intercalate molecules. In this paper, we investigate the effects of charge transfer on some structural parameters in the D_2SO_4-graphite system. Of particular interest is the effect on the nearest-neighbor carbon-carbon bond distance d_{CC} in the graphitic layers. It has been suggested in the past that small changes in d_{CC} on intercalation can be used to determine the magnitude of the charge transfer.[1] A major purpose of our experiment is to experimentally test this idea. The behavior of the graphite-intercalate-graphite interlayer distance in the so-called overcharge regions, in which the stage number remains constant but the charge transfer is constantly increasing, is also of interest. The D_2SO_4-graphite system was selected for these studies because an electrochemical method of intercalation can be used which simultaneously provides precise control of the reaction rate and a natural link to ideas of charge transfer.

Experiment

The intercalation cell was a rectangular cross-section 8×4 mm^2 silica glass tube filled with D_2SO_4, in which an HOPG sample ($20 \times 7 \times 0.2$ mm^3) was held by a platinum clip to serve as the anode, and a bare platinum wire served as cathode. The voltage was monitored while a constant current of 100 µA was passed through the cell. Air intrusion was prevented by a Teflon cap and a constant slight over-pressure of inert gas at the top of the cell. A characteristic electrochemical trace similar to those observed by other workers was obtained.[2] A complete run, in which intercalation proceeded to a saturated stage-1 compound with nominal stoichiometry $C_{21}(DSO_4)(D_2SO_4)_{2.5}$, required about 70 hours.

In situ neutron diffraction measurements were made on a triple-axis spectrometer at the High Flux Isotope Reactor of Oak Ridge National Laboratory, with a neutron wavelength of 2.4 Å and the analyzer crystal set for elastic scattering. The changes in d_{CC} were determined by measuring shifts in the positions of the (100) and (110) graphitic Bragg rings, while the c-axis interlayer spacings were obtained mainly from the (004) stage-1 and (006) stage-2 reflections.

Results and Discussion

The contraction in d_{CC} as a function of time during intercalation is shown in Fig. 1. If one assumes that the nominal charge transfer scale adopted by other workers is correct, i.e., that one electron passed through the external circuit causes one electron to be transferred from a graphitic layer to an intercalate molecule, then one can transform the time scale to a charge transfer scale, as shown at the top of Fig. 1. With this assumption, we find remarkably good agreement with the theory of Pietronero and Strässler up to a charge transfer per carbon atom $f_C = 1/48$, corresponding to a saturated stage-2 compound.
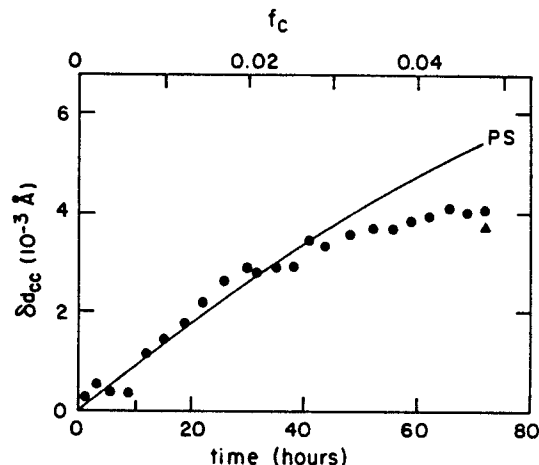

Fig. 1. C-C bond distance contraction δd_{CC} vs. intercalation time or charge transfer per C atom f_C in units of the electronic charge, compared with theory (PS) of Ref. 1.

There are also pronounced contractions[2] along the c-axis in the pure-stage overcharge regions. The effect is shown in Fig. 2 for the stage-1 region. We are attempting to understand the size of the contraction in terms of the balance between short-range repulsive forces and increased interlayer electrostatic attraction due to charge transfer.
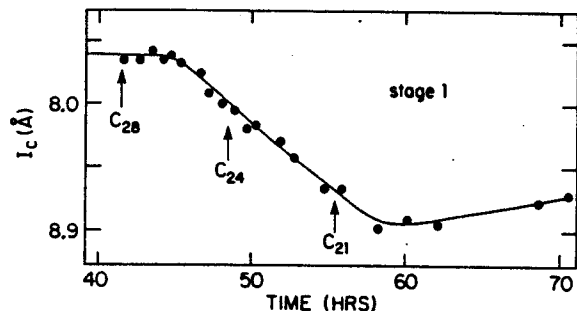

Fig. 2. Contraction of stage-1 graphite-intercalate-graphite interlayer distance I_C, observed during a separate run.

References

1. L. Pietronero and S. Strässler, Phys. Rev. Lett. 47, 593 (1981).

2. B. Bouayad, H. Fuzellier, M. Lelaurin, A. Metrot, and F. Rousseaux, Synthetic Metals 7, 325 (1981), and references therein.